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HIGH PRESSURE RESISTANT THIXOTROPIC EPOXY RESIN ADHESIVE COMPOSITION

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HIGH PRESSURE RESISTANT THIXOTROPIC EPOXY RESIN ADHESIVE COMPOSITION

[Taikohatsuryoku yohensei epokishi jushi settchakuzai soseibutsu]

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[There are no amendments to this patent.]

Claim

A high pressure resistant thixotropic epoxy resin adhesive composition in which for

- (1) 100 parts by weight of epoxy resin having at least two epoxy groups in the molecule,
- (2) a curing agent for epoxy resin,
- (3) 10-200 parts by weight of an inorganic filler having a mean particle diameter in the range of 20-800  $\mu\text{m}$ , and
- (4) 10-200 parts by weight of calcium carbonate the surface of which is treated with either a fatty acid or fatty acid ester are included.

### Detailed explanation of the invention

[0001]

#### Technical field of the invention

The present invention pertains to a high pressure resistant thixotropic epoxy resin adhesive composition. The invention further pertains to a high pressure resistant thixotropic epoxy resin adhesive composition capable of retaining a sufficient adhesive thickness required for adhesion even under a high load and having excellent thixotropy suitable for adhesion of pre-cast concrete subjected to a high load at the time of adhesion.

[0002]

A method of construction where pre-stressed concrete produced by transporting a pre-cast concrete produced in a factory to the construction site, coating an adhesive between the pre-cast concrete and applying post-tension by pressing with a PC steel bar or piano wire has been widely used in recent years. For the adhesive used in this case, mainly two-part epoxy resin adhesives are used. In the aforementioned method of construction, the pre-cast concrete is pressed under a very high load, for example, a load in the range of 20-200 kgf/cm<sup>2</sup>. Thus, when a conventional adhesive is used, the adhesive is pressed out from between the surfaces of the pre-cast concrete being adhered when high pressure is applied and sufficient adhesive does not remain on the surfaces being adhered; thus, retention of sufficient adhesive thickness is difficult. And furthermore, in the aforementioned method of construction, the adhesive is commonly applied to vertical surfaces, and for retention of the adhesive thickness after coating of the adhesive, thixotropy is required. However, when thixotropy is increased upon mixing a thixotropic enhancer in the epoxy resin, the adhesive is likely to escape toward the sides from the adhesive surface when pressure is applied, and retention of sufficient adhesive thickness under a high load while retaining sufficient thixotropy is difficult in known epoxy resin adhesives.

[0003]

#### Problems to be solved by the invention

The purpose of the present invention is to produce a high pressure resistant thixotropic epoxy resin adhesive composition having thixotropy while retaining sufficient adhesive thickness under a high load.

[0004]

#### Means to solve the problem

In other words, the present invention offers a high pressure resistant thixotropic epoxy resin adhesive composition containing (2) a curing agent for the epoxy resin, (3) 10-200 parts by

weight of an inorganic filler having a mean particle diameter in the range of 20-800  $\mu\text{m}$ , and (4) 10-200 parts by weight of calcium carbonate the surface of which is treated with either a fatty acid or fatty acid ester for (1) 100 parts by weight of epoxy resin having at least two epoxy groups in the molecule.

[0005]

Embodiment of the invention

The present invention is explained in further detail below. The high pressure resistant thixotropic epoxy resin adhesive composition (hereinafter referred to as adhesive composition of the present invention) is either a one-part or a two-part epoxy resin adhesive composition capable of retaining thixotropy and with a sufficient adhesive thickness under a high load which has not been possible with the prior art.

[0006]

The type of epoxy resin used in the present invention is not especially limited as long as a polyepoxy compound having at least two epoxy groups in the molecule is used. For example, a glycidyl ether type epoxy resin of bisphenol A and derivatives of same, glycidyl ether type epoxy resin of glycerol, glycidyl ether type epoxy resin of a polyalkylene oxide, glycidyl ether type epoxy resin of phenol novolak, glycidyl ether type epoxy resin of a dimer acid, glycidyl ether type epoxy resin of bisphenol F, and furthermore, epoxy resins having a sulfur atom in the principle chain of the epoxy resin such as Flep 10 [transliteration] of Toray Thiocol Co., Ltd.

[transliteration], etc., can be mentioned. Among those listed above, glycidyl ether type epoxy resin of bisphenol A can be used effectively as an all-purpose epoxy resin. Furthermore, when an epoxy resin having a sulfur atom in the skeleton is used, an excellent adhesion of the composition of the present invention with wet surfaces can be achieved.

[0007]

The curing agent for the epoxy resin used in the present invention is not especially limited as long as a curing agent capable of curing epoxy resins and curing agents commonly used for curing epoxy resin adhesives can be used successfully. For the aforementioned curing agent, curing agents such as amine type curing agents, acid or acid anhydride type curing agents, alkali activated hydrogen compounds, imidazoles, polymercaptan type curing agents, phenolic resins, urea resins, melamine resins and isocyanate type curing agents can be used when the adhesive composition of the present invention is a two-part adhesive composition, and a variety of curing agents such as latent curing agents and ultraviolet curing agents can be used when the adhesive composition is a one-part type.

[0008]

For specific examples of amine type curing agents, aliphatic polyamines such as ethylenediamine, diethylenetriamine and triethylenetetramine; alicyclic polyamines such as isophorone diamine and 1,3-bisaminomethyl cyclohexane; aromatic polyamines such as diaminodiphenyl methane and diaminodiphenyl sulfone; aliphatic polyamines containing an aromatic ring such as methaxylene diamine, etc., can be mentioned. Furthermore, secondary amines and tertiary amines such as amine adduct (polyamine epoxy resin adduct), polyamine-ethylene oxide adducts, ketimine [transliteration], which is a reaction product of an aliphatic polyamine and ketone, straight-chain diamines, tetramethylguanidine, triethanol amine, piperidine, pyridine and benzyl dimethyl amine, and furthermore, liquid polyamides produced by reacting a dimer acid and a polyamine such as diethylenetriamine and triethylenetetramine, etc., can be mentioned.

[0009]

For specific examples of acids or acid anhydride type curing agents, polycarboxylic acids such as adipic acid, azelaic acid and decane dicarboxylic acid; aromatic acid anhydrides such as phthalic anhydride, trimellitic anhydride, ethylene glycol bis(anhydrotrimellitate), glycerol tris(androtrimellitate), pyrromellitic anhydride and 3,3',4,4'-benzophenone tetracarboxylic anhydride; cyclic aliphatic acid anhydrides such as maleic anhydride, succinic anhydride, tetrahydrophthalic anhydride, and methyltetrahydrophthalic anhydride; aliphatic acid anhydrides such as polyadipic anhydride, polyazelaic anhydride, polysebacic anhydride, dodecenyl succinic anhydride and poly(ethyloctadecane dibasic acid) anhydride; halide anhydrides such as chlorend [transliteration] acid anhydride, tetrabrom phthalic anhydride and Het anhydride, etc., can be mentioned.

[0010]

For specific examples of alkali activated hydrogen compounds, dicyandiamide, organic dihydrazide, etc., can be mentioned. For specific examples of imidazoles, 2-methyl imidazole, 2-ethyl-4-methyl imidazole, 2-heptadecyl imidazole, etc., can be mentioned. For specific examples of polymercaptan type curing agents, esters of thioglycolic acids such as pentaerythritol tetrathioglycolate and dipentaerythritol hexathioglycolate, compounds containing a mercapto group such as polysulfide rubber having a mercapto group on the end, etc., can be mentioned. For specific examples of isocyanate type curing agents, isocyanate compounds such as toluene diisocyanate, hexamethylene diisocyanate and xylene diisocyanate, block isocyanate compounds produced by reacting an isocyanate group with phenol, alcohol, caprolactam, etc., for masking, etc., can be mentioned.

[0011]

Furthermore, when the adhesive composition of the present invention is used as a one-part composition, a latent curing agent can be used as a curing agent, and for examples of latent curing agents, ketimine [transliteration], which is a reaction product of an aliphatic polyamine and ketone; triborofluoride-amine complex, which is a compound of an amine such as n-hexylamine, monoethyl amine, benzyl amine, diethyl amine, piperidine, triethylamine and aniline and triborofluoride; dicyandiamide and derivatives of dicyandiamide such as o-tolyl biguanide,  $\alpha$ -2,5-dimethylbiguanide,  $\alpha$ ,  $\omega$ -diphenylbiguanide and 5-hydroxy-naphthyl-1-biguanide; acid hydrazides such as succinic acid hydrazide, isophthalic acid hydrazide, p-oxybenzoic acid hydrazide, salicylic acid hydrazide and phenyl aminopropionic acid hydrazide; diaminomaleonitrile and derivatives of the same; melamine derivatives such as diallyl melamine; amine imides synthesized from carboxylic acid ester, dimethyl hydrazine and epoxy compound; salts of diamine such as piperidine and an aliphatic dicarboxylic acid such as sebacic acid, salts of polyamine such as 2,4,4-trimethyl-2,4,7-trihydroxyfuravane and polyhydroxyphenol such as N,N'-trimethyl-2,3-propane diamine, phenyl phosphonate of polyamine, phenyl phosphate of polyamine; an ester compound of sulfonic acid and primary alcohol, monoester or diester of phosphoric acid or mixtures of the same, an ester compound based on an adduct reaction between sulfonic acid and an epoxy compound, etc., can be mentioned. Furthermore, ultraviolet curing agents such as aromatic diazonium salt and aromatic sulfonate, etc., can be mentioned.

[0012]

The mixing ratio of the curing agent used for curing of the composition of the present invention is preferably in the range of 0.1-1.5 Eq. for the epoxy group included in the epoxy resin, and 0.8-1.2 Eq. is further desirable. When the amount of curing agent included is 0.1 or below of the equivalent of the epoxy group, curing does not occur in the adhesive composition, on the other hand, when the aforementioned equivalent exceeds 1.5, the hardened material produced is brittle.

[0013]

As for the inorganic filler used in the present invention, a variety of materials, for example, fumed silica, sintered silica, sedimented silica, crushed silica, molten silica; iron oxide, zinc oxide, titanium oxide, barium oxide and magnesium oxide; calcium carbonate, magnesium carbonate and zinc carbonate; agalmatolite clay, kaolin clay and baked clay; carbon black, etc., can be mentioned, and the aforementioned inorganic fillers with the exception of those having a uniform spherical shape are used. It is desirable when a filler with an amorphous shape is used as at least one component. Uniform spherical fillers are not desirable since sufficient adhesive thickness cannot be retained under a high load. However, a spherical filler may be used in combination with an

amorphous or flat filler. Furthermore, one type or two or more different types of the aforementioned inorganic fillers may be mixed and used in combination as well. It is desirable when an inorganic filler with a mean particle diameter in the range of 20-800  $\mu\text{m}$  is used in the present invention and 50-500  $\mu\text{m}$  is further desirable. When the mean particle diameter is 20  $\mu\text{m}$  or below, retention of sufficient adhesive thickness is not possible at the time of adhesion as the adhesive composition produced is coated and bonded under load. On the other hand, when the particle diameter exceeds 800  $\mu\text{m}$ , the hardened adhesive composition produced becomes brittle. The mean particle diameter is calculated from the specific surface area obtained by the air permeation method. The mixing ratio of the inorganic filler is in the range of 10-200 parts by weight, preferably in the range of 50-150 parts by weight, for 100 parts by weight of the aforementioned epoxy resin. When the mixing ratio is 10 parts by weight or below, a sufficient adhesion thickness is not possible; on the other hand, when the mixing ratio exceeds 200 parts by weight, the mechanical properties of the hardened adhesive composition such as strength becomes inferior, and furthermore, the thixotropy applied to the aforementioned inorganic filler with the calcium carbonate particle surface treated with either a fatty acid or fatty acid ester described below is inhibited.

[0014]

The calcium carbonate particle surface treated with either a fatty acid or fatty acid ester used in the present invention is used to provide thixotropy to the adhesive composition of the present invention. When adhering is done with an epoxy resin adhesive, in many cases, a coating is applied to the vertical surface, and in this case, it is necessary to provide a sufficient coated thickness after coating and until adhesion. Thus, a calcium carbonate with the surface treated with either a fatty acid or fatty acid ester is mixed to provide thixotropy to the adhesive composition in the present invention. For the fatty acid, straight-chain saturated fatty acids such as lauric acid, myristic acid, palmitic acid, stearic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, montanoic acid, and melissic acid; unsaturated fatty acids such as cetreic acid and sorbic acid; aromatic carboxylic acids such as benzoic acid and phenyl acetic acid, etc., can be mentioned. Among those listed above, palmitic acid and stearic acid are further desirable from the standpoint of thermal stability of the surface treatment and thixotropy. For the fatty acid ester, an ester with a higher fatty acid of at least 8 carbon atoms is desirable, and for example, stearyl stearate, lauryl stearate, stearyl palmitate, lauryl palmitate, glyceride tristearate, glyceride tripalmitate, etc., can be mentioned. Among those listed above, glyceride tripalmitate is especially desirable from the standpoint of thermal stability and thixotropy.

[0015]

As a method used for the surface treatment of the calcium carbonate with the aforementioned fatty acid or fatty acid ester, for example, a method where either a fatty acid or fatty acid ester is either added to calcium carbonate and mixed or sprayed or calcium carbonate is dipped in either a fatty acid or fatty acid ester, adsorption of either a fatty acid or fatty acid ester onto the surface of the calcium carbonate can be made possible. In general, the amount of the either a fatty acid or fatty acid ester used for the treatment is in the range of 1.0-10 wt% for calcium carbonate. The mixing ratio of the calcium carbonate surface treated with either a fatty acid or fatty acid ester is in the range of 10-200 parts by weight, preferably, in the range of 50-150 parts by weight, for 100 parts by weight of the aforementioned epoxy resin. When 10 parts by weight or below, a sufficient thixotropy cannot be achieved and good workability cannot be achieved; on the other hand, when the amount exceeds 200 parts by weight, the specific gravity is increased and viscosity is increased; thus, it is not desirable.

[0016]

In addition to the aforementioned essential components, a suitable amount of materials such as plasticizers, pigments, dyes, anti-aging agents, antioxidants, flame retardants, tackifier resins, dispersants and solvents may be further included in the adhesive composition of the present invention as long as the purpose of the present invention is not lost.

[0017]

For plasticizers that may be used in the present invention, dioctyl phthalate (DOP), dibutylphthalate (DBP); dioctyladipate and isodecylsuccinate; diethylene glycol dibenzoate and pentaerythritol ester; butyl oleate and acetylmethylricenolate; tricresylphosphate and trioctylphosphate; adipic acid propylene glycol polyester and adipic acid butylene glycol polyester, etc., can be mentioned. Furthermore, the aforementioned plasticizers may be used independently or two or more different types of plasticizers may be mixed and used in combination as well.

[0018]

For pigments that may be used in the present invention, inorganic pigments and organic pigments can be mentioned, and for inorganic pigments, titanium dioxide, zinc oxide, ultramarine, red iron oxide, lithopone, lead, cadmium, iron, cobalt, aluminum, chlorate, sulfate, etc., can be mentioned, and for organic pigments used in the present invention, azo pigments, copper phthalocyanine pigments, etc., can be mentioned.



[0019]

For anti-aging agents that may be used in the present invention, compounds such as hindered phenols can be mentioned. For antioxidants that may be used in the present invention, butyl hydroxy toluene (BHT), butyl hydroxy anisole (BHA), etc., can be mentioned. For flame retardants that may be used in the present invention, chloroalkyl phosphate, dimethyl-methylphosphate, bromine-phosphorus compounds, ammonium polyphosphate, neopentyl bromide-polyether, brominated polyether, etc., can be mentioned. For tackifier resins that may be used in the present invention, terpene resins, phenol resins, terpene-phenol resins, rosin resins, xylene resins, etc., can be mentioned.

[0020]

The adhesive composition of the present invention can be formed into a two-part adhesive composition where an epoxy resin and other additives are used for the primary agents and mostly curing agent and other additives used for the curing agent side. Furthermore, the adhesive composition can be formed into a wet-curable type one-part adhesive composition utilizing a latent curing agent. The manufacturing method of the adhesive composition of the present invention used is not especially limited, and it is desirable when each of the aforementioned components is thoroughly kneaded under vacuum using a stirring device such as a mixer and uniformly dispersed to form a composition. In the case of a two-part adhesive, the primary agent and a curing agent are each stored in separate containers and mixed at the time of application.

[0021]

A thixotropic agent is mixed with the aforementioned epoxy resin adhesive to insure a sufficient coating thickness even when coated onto a vertical surface as described above. However, an epoxy resin adhesive with high thixotropy is likely to run under high pressure and retention of sufficient adhesive thickness is difficult. On the other hand, when a filler is mixed with an epoxy resin adhesive, the intermolecular force that provides thixotropy to the epoxy resin is likely to be inhibited; thus, in order to produce an epoxy resin adhesive with high thixotropy, in general, mixing of a filler is not done actively. On the other hand, an inorganic filler having the aforementioned specific mean particle diameter range is actively mixed. When structured as described above, running after coating is absent in the adhesive composition of the present invention based on thixotropy and even when a high load is applied to the adhesive surfaces, the space between adhesive surfaces can be maintained within a suitable range based on the amorphous inorganic fillers mixed with the aforementioned adhesive composition, therefore, the adhesive composition can be successfully retained between the inorganic filler particles and a sufficient adhesive thickness is retained for the adhesive surface. For applications where pre-cast

concrete, etc., is used, for example, when a pre-cast concrete such as culvert box is used to produce high arch road surfaces, underground multi-purpose ducts, gutters, etc., an adhesive thickness of at least 50  $\mu\text{m}$  is desired to achieve sufficient adhesive strength, and the aforementioned adhesive thickness can be achieved in the adhesive composition of the present invention when an inorganic filler is used having a specific range of mean particle diameter. And furthermore, the adhesive composition of the present invention is retained sufficiently between adhesive surfaces and hardened; thus, sealing between pre-cast concrete sections can be achieved, and excellent water tightness can be provided between pre-cast concrete sections.

[0022]

Working examples

The present invention is explained in specific terms below.

#### Working Examples 1-5 and Comparative Examples 1-4

Compounds were mixed at the mixing ratios shown in Table 1 to produce adhesive compositions. For each adhesive composition produced, thixotropy, adhesive strength, and thickness of adhesive were measured and evaluated.

[0023]

Table 1

	① 実 施 例					② 比 較 例			
	1	2	3	4	5	1	2	3	4
③ エポキシ樹脂	100	100	100	100	100	100	100	100	100
④ 硬化剤	24	24	24	24	24	24	24	24	24
⑤ 無機充填剤 A	70	70	50	70	70	70	70	20	
無機充填剤 B	50	70	150						70
無機充填剤 C				70					
無機充填剤 D					70				
無機充填剤 E						30			
無機充填剤 F							150		
無機充填剤 G								70	70
⑥ グレ最小厚さ (mm)	1.0	0.8	0.9	0.8	0.7	0.8	0.9	0.8	0.1
⑦ 4点曲げ試験									
⑧ 圧縮力(500gf/cm <sup>2</sup> )(N/mm <sup>2</sup> )	7.9	8.5	8.8	7.8	7.9	7.1	8.5	7.6	7.8
引張力(200gf/cm <sup>2</sup> )(N/mm <sup>2</sup> )	6.5	7.9	8.6	7.4	6.6	1.5	2.6	1.5	6.5
接着剤厚み ( $\mu\text{m}$ )	50	80	100	30	50	0	10	0	20
⑨ 注中、化合物の単位は重量部である。									

- Key: 1 Working examples  
 2 Comparative examples  
 3 Epoxy resin  
 4 Curing agent  
 5 Inorganic filler \_

- |   |   |
|---|---|
| 6 | Minimum thickness of run [mm]   |
| 7 | 4 point flexure test  |
| 8 | Pressing force (500gf/cm <sup>2</sup> )[N/mm <sup>2</sup> ]<br>Pressing force (200kgf/cm <sup>2</sup> )[N/mm <sup>2</sup> ] |
| 9 | Thickness of adhesive [μm]  |

In the table, the units for the compounds are parts by weight.

[0024]

Components shown in Table

Epoxy resin: YD-128, product of Toto Chemical Co., Ltd.

Curing agent: Epi-Cure H3 [transliteration], product of Yuka Shell Co., Ltd.

Inorganic filler A: Surface treated sedimentation calcium carbonate, mean particle diameter 1 μm or less

Calfine [transliteration] 200: product of Maruo Calcium Co., Ltd.

Inorganic filler B: Heavy calcium carbonate, mean particle diameter 250 μm

T Jutan, product of Maruo Calcium Co., Ltd.

Inorganic filler C: Heavy calcium carbonate, mean particle diameter 20 μm

R Jutan, product of Maruo Calcium Co., Ltd.

Inorganic filler D: Heavy calcium carbonate, mean particle diameter 70 μm

KCN100, product of Maruo Calcium Co., Ltd.

Inorganic filler E: Glass beads, particle diameter 150 μm

Inorganic filler F: Heavy calcium carbonate, mean particle diameter 6.3 μm

Super S, product of Maruo Calcium Co., Ltd.

Inorganic filler G: Heavy calcium carbonate, mean particle diameter 2.2 μm

Super 1500, product of Maruo Calcium Co., Ltd.

[0025]

Minimum thickness of run (thixotropy)

Each adhesive composition produced in the aforementioned working examples and comparative examples was coated onto the entire upper surface of a flat plastic sheet (acrylic sheet) with dimensions of 150 x 150 mm and coated with a release agent ahead of time to a thickness of 1 mm, the coated surface was immediately placed in a vertical position and left standing until curing of the adhesive was achieved under normal conditions. After curing, the

thickness at the minimum adhesive thickness was measured by the micrometer specified in JIS B 7502.

#### 4 point flexure test (adhesive strength)

A piece of cement mortar with a size of 40 x 40 x 80 mm (water cement ratio: 65%, sand cement mass ratio: 2, sand: ISO sand mixed) is used. Each end face of two pieces of the aforementioned cement mortar in the longitudinal direction are used as adhesive surfaces and adhesion is provided with each adhesive composition produced in the aforementioned working examples and comparative examples and instantaneous compression is provided by a compression jig under a compression force of 500 gf/cm<sup>2</sup> and 200 kgf/cm<sup>2</sup>. The adhesive runout is scraped off with a spatula and the bonded pieces are aged at 20°C x 55% RH for 1 week. Using the bonded cement mortar pieces produced, 4 point flexure test is provided according to the method specified in JIS A 6024 at a rate of 2 mm/min to obtain the maximum load and the adhesive strength is calculated. The adhesive strength is calculated according to the equation shown below.

$$F=120 P/bh^2$$

F: Adhesive strength [N/mm<sup>2</sup>]

P: Maximum load [N]

b: Width of test piece (=40 [mm])

h: Height of test piece (=40 [mm])

When the compression force is 200 kgf/cm<sup>2</sup>, adhesive strength of 6 [N/mm<sup>2</sup>] or higher is acceptable.

#### Thickness of adhesive

The cross-section of a test piece ruptured after 4 point flexure test is provided for a test piece compressed under a force of 200 kgf/cm<sup>2</sup> is cut and measured by a microscope. When the compression force is 200 kgf/cm<sup>2</sup>, a thickness of adhesive of at least 50 μm is acceptable.

[0026]

#### Effect of the invention

The adhesive composition of the present invention has thixotropy and even when high load is applied, [run off] from the adhesive surface is absent and a thickness of adhesive required for adhesion can be retained. As a result, high adhesive performance can be maintained even when adhesion is provided under load. Therefore, the adhesive composition of the present invention can be used effectively for construction where a high load is applied, for example, construction where pre-cast concrete pieces such as culvert boxes are bonded and post tension is applied by press with a PC steel bar or piano wire.